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Relation between Eu^{2+} and Ce^{3+} f \leftrightarrow d-transition energies in inorganic compounds

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Abstract

Data available on the fd-transition energies of Ce^{3+} in inorganic compounds are compared with those of Eu^{2+} in the same compounds. Despite differing charge compensating defects, clear correlation was found. The redshift of absorption, the Stokes shift of emission, the centroid shift of the 5d configuration and the total crystal field splitting of the 5d levels of Eu^{2+} and Ce^{3+} all appear to be linearly related to one another. The values for Eu^{2+} are about 0.7 times those for Ce^{3+} . This implies that spectroscopic properties known for Ce^{3+} can be employed to roughly predict spectroscopic properties for Eu^{2+} and vice versa. The findings for Ce^{3+} and Eu^{2+} can be generalized to all trivalent and divalent lanthanides.

1. Introduction

The energy difference $E(n, Q, A)$ between the lowest level of the $[\text{Xe}]4f^n$ configuration of a divalent or a trivalent lanthanide ion and the lowest level of the $[\text{Xe}]4f^{n-1}5d^1$ configuration depends on the number n of electrons in the $4f^n$ ground state, the ionic charge Q and the compound, represented by the variable A . The following empirical relationships hold [1–4]:

$$E_{\text{abs}}(n, Q, A) = E_{\text{Afree}}(n, Q) - D(Q, A) \quad (1)$$

$$E_{\text{em}}(n, Q, A) = E_{\text{Afree}}(n, Q) - D(Q, A) - \Delta S(Q, A), \quad (2)$$

where $E_{\text{Afree}}(n, Q)$ is for each lanthanide ion a constant and close to the energy of the first fd transition in the free ion. $D(Q, A)$ and $\Delta S(Q, A)$ are the redshift and Stokes shift in compound A . The redshift is the lowering of the lowest $4f^{n-1}5d$ level relative to the E_{Afree} -value due to the interaction with the crystal field. After fd excitation, the level is further lowered by the Stokes shift due to lattice relaxation.

These equations are valid for all types of compound (fluorides, chlorides, bromides, iodides, oxides and sulfides) and in principle also for glasses and organic materials. The

interaction between the 5d electron and its environment appears not to depend much on the number of electrons in the 4f shell, and a single parameter can be used to describe the effect on the lowest 5d level. This redshift parameter and its relation to type of compound was studied in detail for Ce^{3+} . It can be written as [5–8]

$$D(3+, A) = \epsilon_c + \frac{\epsilon_{\text{cfs}}}{r(A)} - 0.234 \text{ eV}, \quad (3)$$

where the centroid shift ϵ_c is defined as the shift of the barycentre energy of the 5d configuration of Ce^{3+} relative to the free ion value (6.352 eV). The total crystal field splitting ϵ_{cfs} is the energy difference between the lowest and highest energy 5d state. $r(A)$ determines the fraction of ϵ_{cfs} that contributes to the redshift.

For the divalent lanthanides, a relationship similar to equation (3) is expected. However, it cannot be established as easily as was done for Ce^{3+} . One could use La^{2+} , that has the same electron configuration as Ce^{3+} , but La^{2+} is rarely stable in compounds and apart from some fluorides spectroscopic information is not available. Eu^{2+} seems to be the only candidate ion to test equation (3) for divalent lanthanides. In this work spectroscopic information on Eu^{2+} in compounds providing sites of octahedral symmetry is used to derive an expression similar to equation (3).

The major part of this work is concerned with a comparison of the transition energy $E(7, 2+, A)$ for Eu^{2+} in a compound with the energy $E(1, 3+, A)$ for Ce^{3+} in that same compound. Eu^{2+} is used as a representative for the divalent lanthanides because it is by far the most widely studied divalent lanthanide ion and much information is available [4]. Comparison of Eu^{2+} with Ce^{3+} was done for a small number of compounds before [9, 10]. Here it is done for a much larger number of compounds and it will be shown that both energies are linearly related to each other. This implies that redshift, Stokes shift, centroid shift and crystal field splitting must also be linearly related. Once the linear relationships are established, a tool is obtained to predict emission and absorption wavelengths of the divalent lanthanides from information available on trivalent lanthanides and vice versa.

2. Results and discussion

Data for Eu^{2+} on $E_{\text{abs}}(7, 2+, A)$ together with the experimental error and data on $E_{\text{em}}(7, 2+, A)$ can be found in [4]. Data on $E_{\text{abs}}(1, 3+, A)$ and $E_{\text{em}}(1, 3+, A)$ for Ce^{3+} were published in [2]. Whenever data are available on Eu^{2+} as well as on Ce^{3+} in the same compound and at the same site they can be displayed against each other, as has been done in figure 1. A clear correlation exists between the transition energy in Eu^{2+} and that in Ce^{3+} . A linear least squares fit through all the data (110 data points) yields

$$E(7, 2+, A) = (0.64 \pm 0.02)E(1, 3+, A) + (0.53 \mp 0.06) \text{ eV}. \quad (4)$$

The result is shown as the solid line drawn through the data.

95% of the data in figure 1 pertain to Eu^{2+} and Ce^{3+} on divalent cation sites. This means that in the case of Ce^{3+} a charge compensating defect is present. Usually it is located beyond the first anion coordination sphere. Apparently its effect on the transition energy is smaller than ± 0.18 eV, otherwise data would scatter more strongly around the drawn line. However, when charge compensation is by means of an anion in the first coordination shell, effects are much stronger. This can be the situation in $\text{NaF}:\text{Ce}^{3+}$ where two oxygens on neighbouring fluorine sites may act as charge compensators [5, 11, 12]. Such data deviate strongly in figure 1 and are not displayed.

Compounds may possess inequivalent cation sites. Then, when Eu^{2+} shows preference for occupation of a different site than Ce^{3+} , large deviations may occur. For example in BaY_2F_8 ,

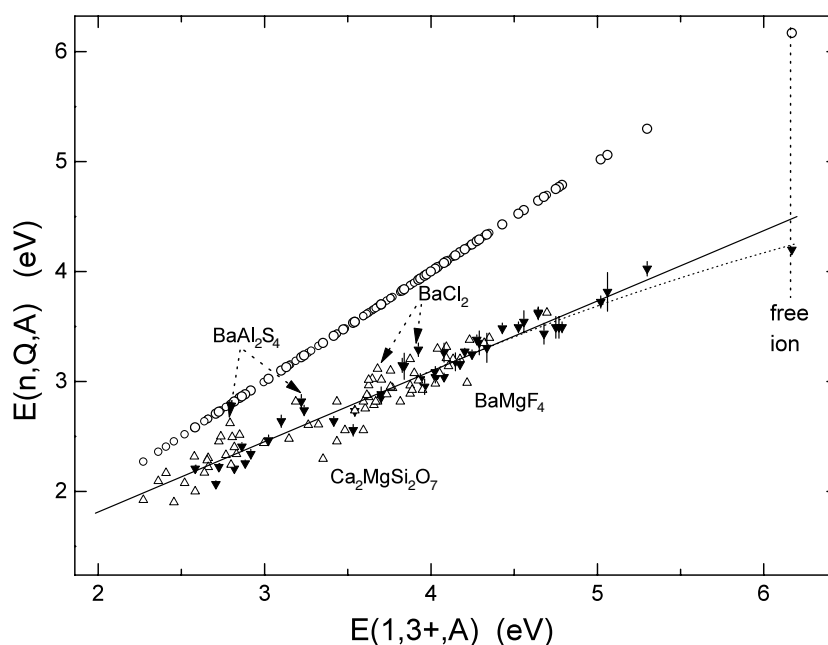


Figure 1. ▼, energy $E_{\text{abs}}(7, 2+, A)$ of the first fd transition in Eu^{2+} against the energy $E_{\text{abs}}(1, 3+, A)$ of that of Ce^{3+} . △, energy of $E_{\text{em}}(7, 2+, A)$ against $E_{\text{em}}(7, 2+, A)$ for Ce^{3+} . ○, data for Ce^{3+} displayed against themselves.

Eu^{2+} occupies the Ba site and Ce^{3+} the Y site. If it were shown in figure 1, the data point would deviate by 0.64 eV. For the same reason, data on Ce^{3+} and Eu^{2+} in CaLa_2S_4 were not used in figure 1. In compounds like SrAlF_5 , CaAl_2O_4 , $\text{CaAl}_2(\text{SiO}_4)_2$ and SrAl_2S_4 , different divalent cations sites are present. The small Ce^{3+} ion may prefer to occupy a different site than the larger Eu^{2+} ion. Again this may translate to large deviations. Data on these compounds are also not shown in figure 1.

Figure 1 shows that the fd-transition energy in Eu^{2+} is a factor of 0.64 less strongly influenced by the crystal field than that in Ce^{3+} . This implies that Stokes shift, redshift, crystal field splitting and centroid shift for Eu^{2+} and Ce^{3+} should also be approximately linearly related. For the Stokes shift this is demonstrated in figure 2. The errors in the Stokes shift for Eu^{2+} are shown. That of Ce^{3+} is typically ± 0.05 eV. The Eu^{2+} Stokes shift appears 0.61 ± 0.03 times that of Ce^{3+} , which agrees with predictions from equation (4).

The data on Stokes shift in BaMgF_4 deviate significantly and the emission also shows relatively large deviation in figure 1. For the wavelength of Ce^{3+} df emission to the $^2\text{F}_{5/2}$ ground state in BaMgF_4 , a value of 294 nm from Yamaga *et al* [13] was used. It was measured for a Czochralski grown crystal with Na^+ added as charge compensating defect. The same authors report an emission at 308 nm when the crystal is grown without codoping using the Bridgman technique. Results are more consistent when the 308 nm emission is used. The above example demonstrates that a comparison between Ce^{3+} and Eu^{2+} spectroscopic data may help in the interpretation and judgement of the quality of data. It appears that deviating data often belong to compounds with large Ba sites. $\text{BaAl}_{10.67}\text{O}_{17}$ is deviating in figure 2. Emission and absorption data on BaAl_2S_4 and $\alpha\text{-BaCl}_2$ deviate relatively strongly in figure 1.

Combining equations (4), (1) and (2) using $E_{\text{Afree}}(7, 2+) = 4.216$ eV and $E_{\text{Afree}}(1, 3+) = 6.118$ eV one obtains

$$D(2+, A) = 0.64D(3+, A) - 0.233 \text{ eV} \quad (5)$$

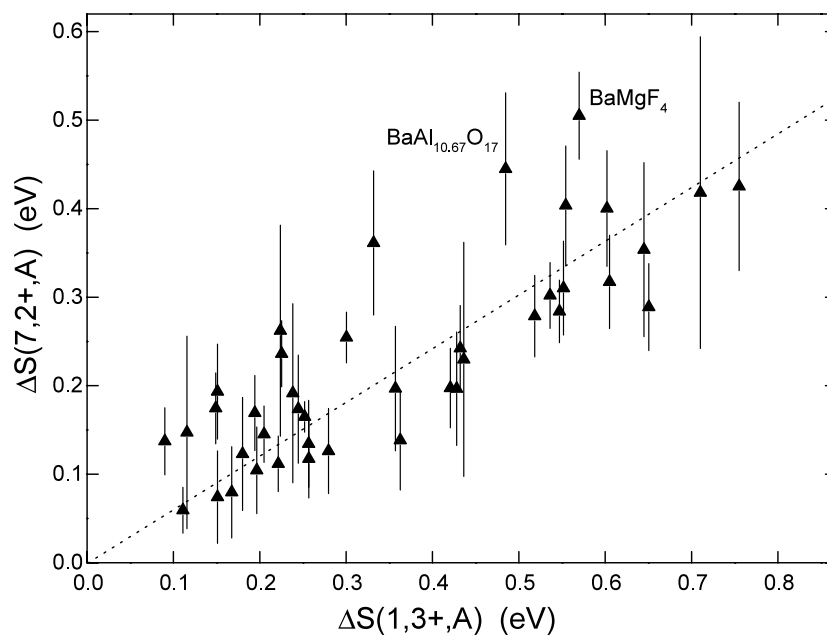


Figure 2. The Stokes shift $\Delta S(7, 2+, A)$ of Eu^{2+} emission against the Stokes shift $\Delta S(1, 3+, A)$ of Ce^{3+} emission. The dashed line is from a linear least squares fit through zero.

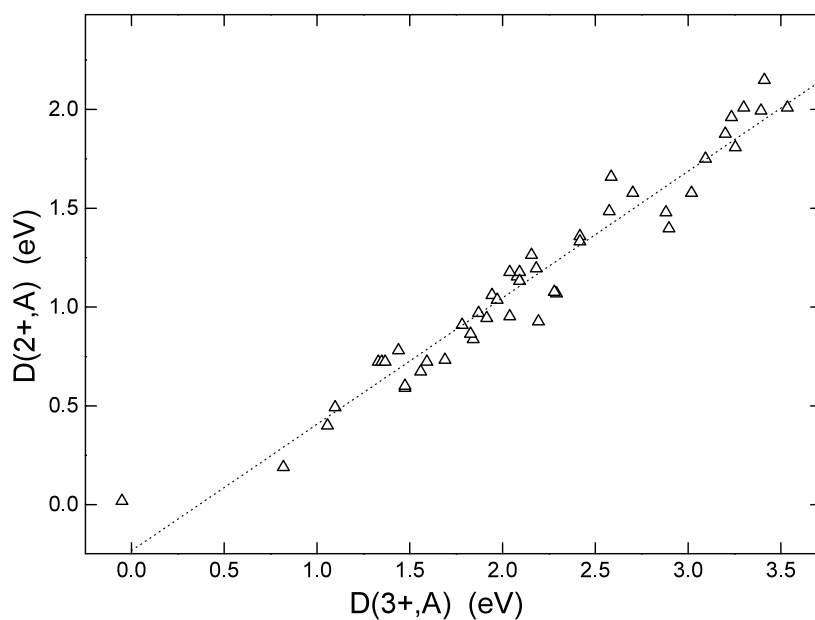


Figure 3. The redshift $D(2+, A)$ for the fd transition of Eu^{2+} in compounds against that of Ce^{3+} .

as a linear relationship between redshift in the divalent and the trivalent lanthanides. Data on the redshift of the fd transition in Eu^{2+} versus Ce^{3+} together with the line expressed by equation (5) are shown in figure 3.

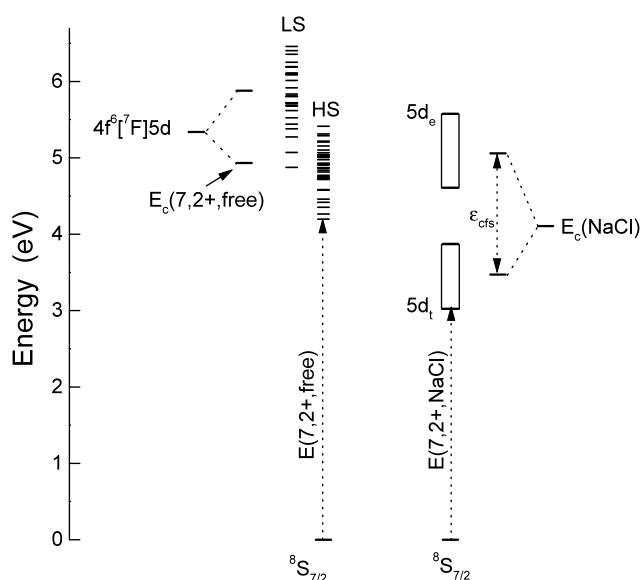


Figure 4. The HS and LS $4f^6[7F]5d$ energy levels of free Eu^{2+} . The right-hand side shows the level energies for Eu^{2+} in NaCl.

To test whether centroid shift and crystal field splitting are linearly related, information is needed on both parameters for Ce^{3+} as well as for Eu^{2+} . Values on ϵ_{cfs} and ϵ_c are available for Ce^{3+} in about 80 different compounds [5–8]. Information on Eu^{2+} is less abundant and more difficult to obtain. Figure 4 shows the $4f^6[7F]5d$ energy levels of free Eu^{2+} [14]. The degeneracy weighted average level position is at 5.338 eV. The exchange interaction separates the high spin (HS) states from the low spin (LS) states with average energy at 4.932 and 5.880 eV, respectively. Spin–orbit interaction and other interactions finally create the rich level structure of free Eu^{2+} [14]. The transitions from the $^8S_{7/2}$ ground state to the HS states between 4.2 and 5.4 eV are spin and dipole allowed; those to the LS states are spin forbidden.

The right-hand side of figure 4 illustrates the situation for Eu^{2+} in NaCl. The octahedral crystal field splitting creates a splitting into triplet $4f^6[7F]5d_t$ and doublet $4f^6[7F]5d_e$ levels. The spin-allowed transitions are observed as two approximately 0.74 eV broad bands in optical excitation, absorption or reflection spectra. The energy difference between the barycentres of these bands is the $10Dq$ crystal field splitting [15]. We define this as the total crystal field splitting $\epsilon_{\text{cfs}}(7, 2+, \text{NaCl})$ of Eu^{2+} in NaCl. In practice, $\epsilon_{\text{cfs}}(7, 2+, A)$ can only be obtained for compounds providing sites of octahedral symmetry, i.e., sites with octahedral, cubal or cuboctahedral coordination. Lower symmetry sites yield a splitting in more than two 5d bands. Since the bands are very broad they overlap strongly and merge into one broad continuum preventing accurate determination of the total crystal field splitting.

The centroid shift in Eu^{2+} can be defined as

$$\epsilon_c(7, 2+, A) = E_c(7, 2+, \text{free}) - \left(E(7, 2+, A) + 0.37 + \frac{\epsilon_{\text{cfs}}(7, 2+, A)}{r(A)} \right) \text{ eV} \quad (6)$$

where $r(A)$ is 5/2 for octahedral sites and 5/3 for cubal and cuboctahedral sites. The value of 0.37 eV accounts for the difference between $E(7, 2+, A)$ and the barycentre energy of the 0.74 eV wide first $4f^6[7F]5d$ band in spectra, see figure 4. $E_c(7, 2+, \text{free}) = 4.93$ eV is the barycentre energy of the HS $4f^6[7F]5d$ levels in free Eu^{2+} .

Table 1. 5d crystal field splitting ϵ_{cfs} and centroid shift ϵ_c in Eu^{2+} on sites of octahedral symmetry. Energies are in electronvolts. f is the ratio $\epsilon_c(7, 2+, A)/\epsilon_c(1, 3+, A)$. Estimated values or data that require further experimental verification are given within brackets.

Compound	ϵ_{cfs}	ϵ_c	f	f^*	References
Octahedral					
KF	2.06	0.49			[15]
NaF	2.27	0.34			[15]
LiCaAlF ₆ ^a	2.13	0.19	7		[25, 26]
MgF ₂ :Yb ^a	3.13	0.29			[27]
CsCaF ₃	2.54	0.63			[28]
RbCaF ₃	2.29	0.54			[29]
KCaF ₃	2.70	0.23			[29]
RbCl	1.41	0.81			[30]
KCl	1.49	0.87			[15]
NaCl	1.59	0.90			[31, 32]
RbBr	1.39	0.85			[30]
KBr	1.36	0.88			[15, 33]
NaBr	1.46	0.95			[15]
RbI	1.12	0.91			[15]
KI	1.18	0.99			[15]
NaI	1.32	1.02			[15]
SrS	1.49	1.71	(0.64)	(0.75)	[20]
CaS	1.86	1.75	(0.62)	(0.72)	[18, 20]
MgS	1.74	1.66	0.58	0.68	[17, 19]
CaSe	1.56	1.71	(0.60)	(0.70)	[18, 20]
Cubal					
BaF ₂	1.74	0.27	0.34	0.68	[34, 35]
SrF ₂	1.84	0.30	0.34	0.64	[34, 35]
CaF ₂	2.05	0.27	0.30	0.6	[35]
CsI	1.03	0.98			[36]
SrCl ₂	1.33	0.62	0.37	0.53	[37]
Cuboctahedral					
BaLiF ₃	0.87	0.32	0.39	0.73	[38]
RbMgF ₃	0.81	0.43			[39]
KCaF ₃	(0.56)	(0.23)			[29]
KMgF ₃	0.87	0.01	0.03	0.54	[39, 40]
BaZrO ₃	(0.78)	(1.43)			[41]

^a These compounds have distorted octahedral coordination.

Table 1 compiles data on the crystal field splitting of Eu^{2+} in compounds at sites of O_h symmetry. The centroid shift was calculated with equation (6) using values for $E(7, 2+, A)$ compiled in [4]. For MgF_2 it was assumed that the crystal field splitting for Eu^{2+} is the same as the energy difference between the $4f^{13}[{}^7F_{7/2}]5d_e$ and $4f^{13}[{}^7F_{7/2}]5d_t$ levels of Yb^{2+} in MgF_2 . It is well known that in the alkali halides Eu^{2+} tends to aggregate; see the references in table 1. Care was taken to select data on isolated Eu^{2+} centres. For the compounds providing cuboctahedral coordination, occasionally the spectra were interpreted differently than in the original papers. More information on this can be found elsewhere [16]. For MgS , SrS , CaS and CaSe the spectra are also differently interpreted.

$\text{MgS}:\text{Eu}^{2+}$ was studied in detail by Asano and Nakao [17, 18] and later by Yamashita and Takagoshi [19]. Originally, the so-called C band at 250 nm in the excitation spectrum of Eu^{2+} luminescence was assigned to the transition to the e-doublet state [18]. However, following

Yamashita *et al* [20], the C band should be assigned to the fundamental absorption. It seems more likely that the so-called B band is the sought e doublet. There are two main arguments in favour of this assignment. (1) The intensity of the B band scales with Eu concentration. (2) A $10Dq$ -value of 1.74 ± 0.25 eV is obtained which is in line with expectations based on Eu²⁺ doped alkali halides.

Also for CaS and CaSe, we attributed the C band observed by Nakao [18] to host lattice excitation [20]. The additional excitation band at energies just lower than the fundamental absorption, i.e., the B band in the work by Nakao, is attributed to the transitions to the e doublet. $10Dq$ -values of 1.86 ± 0.25 and 1.56 ± 0.19 eV are estimated for CaS and CaSe respectively.

There are seven compounds from table 1 for which the crystal field splitting of the 5d configuration of Ce³⁺ is known. Display as in figure 5 reveals that ϵ_{cfs} in Eu²⁺ is 0.77 times that in Ce³⁺, and not 0.64 as in equation (4). There is other evidence that a ratio of 0.77 applies. Figure 6 shows the crystal field splitting of Eu²⁺ of the compounds in table 1. Similar figures for Ce³⁺ can be found elsewhere [8, 16]. The dashed curves through the data are given by

$$\epsilon_{\text{cfs}} = \beta_{\text{poly}}^Q R_{\text{av}}^{-2} \quad (7)$$

where β_{poly}^Q is a constant that depends on the type of coordination polyhedron and whether the lanthanide is Ce³⁺ with $Q = 3+$ or Eu²⁺ with $Q = 2+$. R_{av} is defined as

$$R_{\text{av}} = 1/N \sum_{i=1}^N (R_i - 0.6\Delta R). \quad (8)$$

R_i (pm) are the bondlengths to the N coordinating anions in the unrelaxed lattice. $\Delta R = R_M - R_{\text{Ln}}$ with R_M the ionic radius of the cation that is replaced by the lanthanide Ln with ionic radius R_{Ln} . For both Eu²⁺ and Ce³⁺, the ratio $\beta_{\text{octa}}^Q : \beta_{\text{cubal}}^Q : \beta_{\text{cubo}}^Q$ equals 1:0.89:0.42 [16]. From comparing Eu²⁺ data with Ce³⁺ data it follows that $\beta_{\text{poly}}^{2+} = 0.81 \beta_{\text{poly}}^{3+}$. If one also takes the 12 pm larger size of Eu²⁺ into account, equation (7) yields $\epsilon_{\text{cfs}}(7, 2+, A) = 0.77\epsilon_{\text{cfs}}(1, 3+, A)$, i.e., a ratio which is the same as observed in figure 5. It is concluded that the crystal field splitting in Eu²⁺ is 0.77 times the value for Ce³⁺.

For several of the compounds in table 1 the centroid shift both in Eu²⁺ and in Ce³⁺ is known. Values for the centroid shift of Ce³⁺ 5d levels can be found in [5, 6, 8]. For Ce doped SrS, CaS and CaSe the high energy e doublet was not observed because of host lattice absorption [22, 23]. Yet, its position can be estimated using the ratio of 0.77 found above, and from that the centroid shift of Ce³⁺ was estimated.

The ratio f between the centroid shift of Eu²⁺ and Ce³⁺ is compiled in table 1. It appears significantly smaller than the ratio between the crystal field splitting in Eu²⁺ and Ce³⁺. Furthermore, f is almost zero for KMgF₃ and increases from ≈ 0.35 for fluorides to ≈ 0.6 for sulfides. Apart from an estimated stochastic error of at most 0.1, a systematic error can be present in f due to an incorrect method of calculating ϵ_c with equation (6). To demonstrate this, ϵ_c and f were recalculated employing 5.21 eV as the effective barycentre energy $E_c(7, 2+, \text{free})$ for free Eu²⁺. All centroid shift values for Eu²⁺ are then augmented by 0.28 eV. The newly obtained ratios f^* in the fifth column of table 1 fall around 0.65 ± 0.1 . This ratio is still smaller than observed for the crystal field splitting and about the same as in equation (4). At this stage it is concluded that the centroid shift in Eu²⁺ is 0.4–0.7 times the value in Ce³⁺ where the factor possibly depends on the type of compound.

There is another method to determine the ratio between centroid shift in Eu²⁺ and Ce³⁺. One may write for the redshift of the fd absorption in Eu²⁺

$$D(2+, A) = f\epsilon_c(3+, A) + 0.77 \frac{\epsilon_{\text{cfs}}(3+, A)}{r(A)} - c + [0.61\Delta S(3+, A)] \quad (9)$$

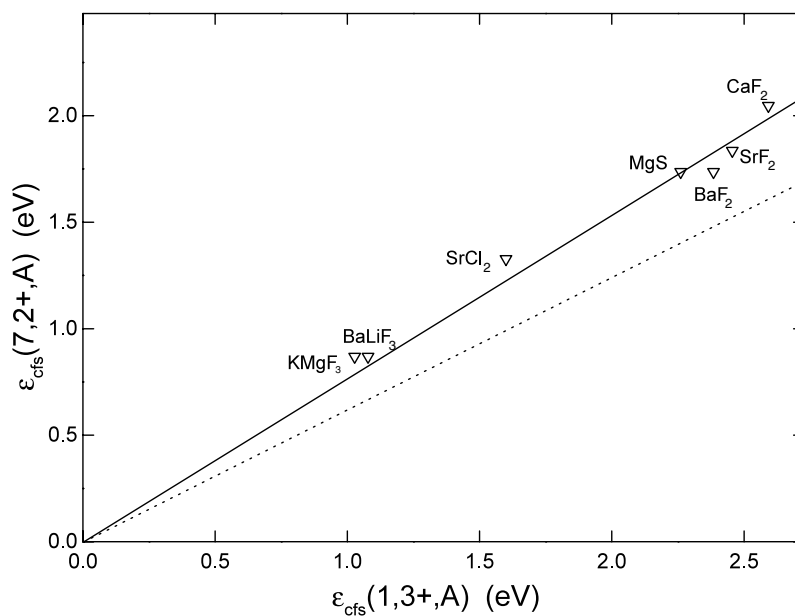


Figure 5. $\epsilon_{\text{cfs}} \equiv 10Dq$ of the $\text{Eu}^{2+}4f^65d$ configuration in compounds at sites of O_h point symmetry against ϵ_{cfs} for Ce^{3+} in the same compounds. The dashed line has a slope of 0.64 and the solid line is from a linear least squares fit through zero with slope 0.77. Data on $\text{MgS}:\text{Ce}^{3+}$ are obtained from [21]. Data on the other Ce^{3+} doped compounds can be found in [5, 6, 8].

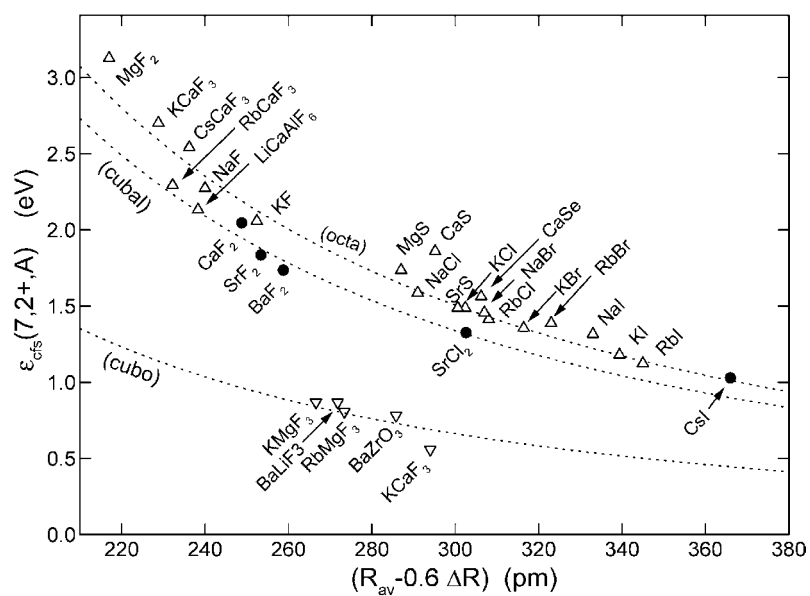


Figure 6. Crystal field splitting of the $4f^65d$ configuration of Eu^{2+} at sites of O_h point symmetry against the average distance to the nearest anion ligands.

where the Stokes shift can be added when dealing with df emission. $\epsilon_c(3+, A)$, $\epsilon_{\text{cfs}}(3+, A)$, and $\Delta S(3+, A)$ are known for Ce^{3+} in 80 different compounds (fluorides, chlorides, bromides,

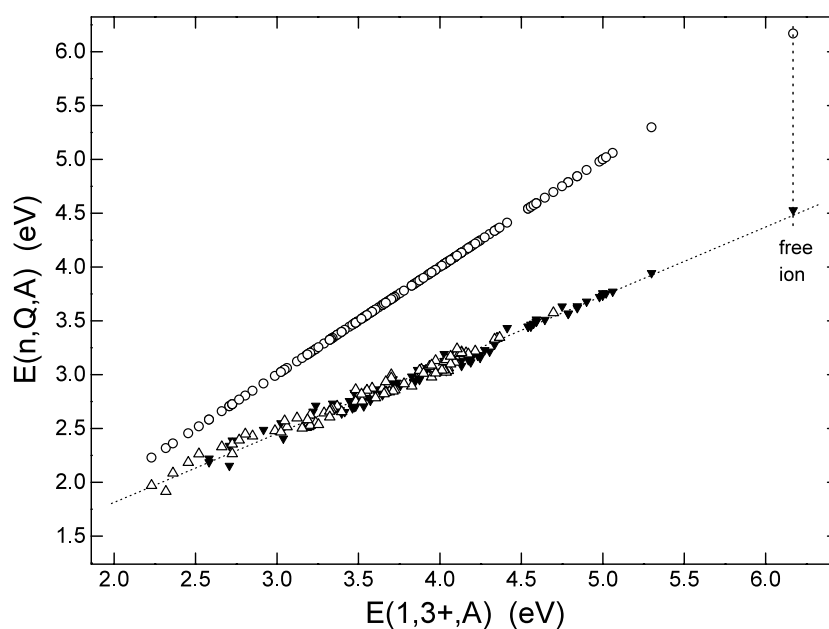


Figure 7. ▼, energy $E_{\text{abs}}(7, 2+, A)$ of the first fd absorption in Eu^{2+} calculated from $E_{\text{abs}}(1, 3+, A)$ observed for Ce^{3+} . Δ, energy $E_{\text{em}}(7, 2+, A)$ of df emission in Eu^{2+} calculated from $E_{\text{em}}(1, 3+, A)$ observed for Ce^{3+} . O, data for Ce^{3+} displayed against itself.

oxides and sulfides) [5–8]. These data can be used to calculate $D(2+, A)$ of Eu^{2+} using f and c as adjustable parameters. These constants are to be determined from requiring that values for $E(7, 2+, A)$ calculated with equation (1) and equation (2) should follow (4) as closely as possible. In other words f is adjusted until the slope of 0.64 in equation (4) is obtained. The results are shown in figure 7 where a best match is obtained for $f = 0.61$ and $c = 0.453$ eV. The dashed line through the simulated data is constructed using equation (4). It is now concluded that the centroid shift in Eu^{2+} is on average 0.61 times that in Ce^{3+} .

It was recently found that there are two separate contributions to the centroid shift

$$\epsilon_c = \epsilon_1 + \epsilon_2 \quad (10)$$

where ϵ_1 is a contribution due to the covalence between 5d and ligand orbitals and ϵ_2 is a contribution from the correlated motion between 5d electron and ligand electrons. ϵ_2 is most important for ionic compounds like fluorides, phosphates and sulfates. ϵ_1 is most important in covalent compounds like chlorides, bromides and sulfides [24]. We assumed in equation (9) that f is the same for ϵ_1 and ϵ_2 . However, the f -values in table 1 actually suggest that f is smaller for the ionic fluoride compounds, i.e., it is smaller for ϵ_2 . If such variability of f with the ionicity of the compound indeed occurs, it will introduce a slight deviation from linear behaviour. This may be the reason that equation (4) does not extrapolate towards the proper free ion value; see figure 1. The dashed line tentatively illustrates the possible non-linear effect.

Since the crystal field splitting in Eu^{2+} is 0.77 times that of Ce^{3+} , but the centroid shift and Stokes shift is 0.61 times as large, dispersion from equation (4) is unavoidable. This is already evident in figure 7 where the data scatter with a standard deviation of 0.06 eV from the drawn line. This, together with the standard deviation of 0.08 eV from experimental errors, already explains 80% of the observed 0.12 eV standard deviation in figure 1. Additional contributions

may arise from charge compensating defects or when excessive relaxation occurs around a lanthanide ion on a much too large or a much too small site. Another consequence of the different ratios is that data on compounds providing large crystal field splitting (Ca sites) tend to fall below the straight line in figure 7, and data on crystals providing small crystal field splitting (Ba sites) above.

It is now concluded that if (1) Eu^{2+} occupies the same site as Ce^{3+} , (2) the charge compensating defect is located beyond the first anion coordination shell and (3) excessive lattice relaxation does not take place, then $E(7, 2+, A)$ can be predicted with standard deviation ± 0.12 eV from Ce^{3+} data and $E(1, 3+, A)$ can be predicted with standard deviation ± 0.2 eV from Eu^{2+} data. Whenever Eu^{2+} data deviate by more than ≈ 0.25 eV this may be related to one of the above causes, to an erroneous interpretation of data or to erroneous experimental data. This latter situation probably applies to $\text{Ca}_2\text{MgSi}_2\text{O}_7$; see figure 1.

3. Summary and conclusions

In this work the energy of the fd transition in Eu^{2+} at a site in a compound has been compared with that of Ce^{3+} at the same site in the same compound. The transition energy in Eu^{2+} is in good approximation linearly related to that in Ce^{3+} ; see equation (4). The same applies to the energy of the df emission. For this to hold, a similar linear relationship should apply to the Stokes shift, centroid shift and crystal field splitting. Data available on the Stokes shift plotted in figure 2 indeed reveal a linear relationship. The Stokes shift for Eu^{2+} is 0.61 ± 0.03 times the value for Ce^{3+} .

To test linear relationships for the centroid shift and crystal field splitting, data have been collected on the fd transitions of Eu^{2+} in compounds providing sites of octahedral symmetry. The crystal field or $10Dq$ splitting in Eu^{2+} appears to be 0.77 times that in Ce^{3+} ; see figure 5. A similar conclusion was drawn from the ratio in β_{poly} values for divalent and trivalent lanthanides; see equation (7) and figure 6. From the results in table 1 and also from the simulation in figure 7 and equation (9), the centroid shift in Eu^{2+} is found to be on average 0.61 times that of Ce^{3+} . However, there are indications that this value scales with the ionicity of the compounds, and it may be smaller in fluorides.

The relationships found help in predicting spectroscopic properties for Eu^{2+} from properties known for Ce^{3+} and vice versa. Provided that (1) Eu^{2+} occupies the same site as Ce^{3+} , (2) the charge compensating defect is located beyond the first anion coordination shell and (3) the lattice relaxation around Eu^{2+} is not too different from that around Ce^{3+} , redshift values of Eu^{2+} can be predicted with standard deviation of about ± 0.12 eV from Ce^{3+} . Redshift values for Ce^{3+} can be predicted with about ± 0.2 eV accuracy from Eu^{2+} data. Besides the fact that the relationships found help in predicting spectroscopic properties, they may also be used to signal erroneous data or to provide clues to the nature of charge compensating defects and lattice relaxation.

The theory behind the 0.6–0.8 times smaller crystal field splitting, Stokes shift and centroid shift in Eu^{2+} as compared to Ce^{3+} was not addressed in this work. However, since this factor does not depend on the type of compound, it is already clear that it must be an intrinsic property of divalent and trivalent lanthanides.

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